

MINERALOGICAL INVESTIGATION OF RED BOLES IN DECCAN BASALT NEAR
PUNE (MAHARASHTRA)

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

by

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ANIL DUTT SHUKLA

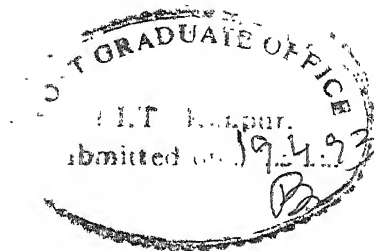
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CERTIFICATE

This is to certify that the present work, entitled "Mineralogical Investigation of Red Boles in Deccan Basalt near Pune (Maharashtra)" has been carried out by Mr. Anil Dutt Shukla under my supervision and it has not been submitted elsewhere for a degree.

A handwritten signature in cursive script, reading "Bikash C. Raymahashay".

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ABSTRACT

Samples were collected from red layers sandwiched between Deccan basalt flows in the type area near Pune. The physical features and mineralogy of two profiles - one near Shirwal on Pune - Satara road and the other near Saswad on Pune-Solapur road differ in details. The red layer at Shirwal is relatively hard and is extensively cemented by veins of quartz and zeolite. The zeolite was identified to be of heulandite composition. Sharp peaks of quartz and zeolite in the red bole material distinguish it from a dark top soil developed over the upper basalts. The material between basalt flows in the Saswad area by contrast is mostly unconsolidated and granular. At least in one outcrop, the colour is brown, rather than red. There is no distinctive abundance of quartz and zeolite in these horizons.

A glycol expansive smectite is common in both areas in the soil and weathered basalt as well as in the red/brown boles. This mineral is likely to be a product of low temperature weathering of Ca-plogioclase (bytownite), augite and heulandite. Ground water composition from Pune area plots near the heulandite - Ca smectite boundary in thermodynamic stability diagrams. The absence of kaolinite in the weathering products indicates relatively high silica activity.

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April 1993
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Anil Dutt Shukla

Dedicated to my beloved parents

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CHAPTER 1

INTRODUCTION AND OBJECTIVE

The large outcrop of volcanic igneous rocks of basaltic composition occurring in Central and Western India is well known in Indian geology as the Deccan Basalt Province. This area has been the site of detailed geologic investigation as well as several important civil engineering projects. Weathering of Deccan basalt into expansive soil has drawn the attention of engineering geologists for a long time. However, during detailed field work in the basalt country, a peculiar red horizon interbedded with the massive basalt flow units has also assumed importance both from geological and civil engineering points of view. This material, collectively called 'Red Bole', is neither an intertrappean sedimentary bed nor typical residual soil. Therefore, several conflicting ideas have developed regarding its origin. On the other hand, being relatively weathered and weak in strength, red boles create lack of homogeneity within basalt as foundation material. Therefore, a clear idea about its origin and occurrence is important for civil engineers.

With this background, it was decided to undertake a detailed mineralogical study of red boles in the type area and compare their characteristics with recent residual soil. The Pune area was selected because of the availability of previous work on weathering and soil formation as well as easy accessibility for road cuts/ghat sections where complete profiles could be studied.

The main objectives of this thesis project can be listed as follows:

1. Selection of complete profiles exposing a minimum of four horizons, namely, a) lower basalt flow, b) red bole layer overlying the lower basalt, c) upper basalt flow, and d) top soil on the upper basalt.
2. Measurement and characterization of such profiles on a large scale.
3. Collection of representative rock and soil samples from all horizons for subsequent laboratory study.
4. Study of rock samples in hand specimens, thin sections and by X-ray diffraction.
5. Determination of soil mineralogy by X-ray diffraction.
6. Determination of some important index properties of red bole and recent soil like soil pH, organic matter content, cation exchange capacity (CEC) and major element composition.
7. Utilization of available geochemical information and thermodynamic data to work out the stability of minerals in the weathering environment.
8. Evaluation of existing hypotheses about origin of red boles in the light of field and laboratory data collected from the study area.

CHAPTER 2

LITERATURE REVIEW

2.1 Deccan Volcanism:

A vast area of the order of half a million (512000) Sq. Km. in the Western and Central part of India is covered by basaltic lava flows. These rocks are famous in Indian geology as the Deccan Basalts because of their geographic location (Fig. 2.1). With frequently occurring flat-topped landforms the rocks are classified as Plateau Basalts. The step like appearance in vertical sections has also given them the name Deccan Traps, the term being of Scandinavian Origin (Krishnan, 1968). The lava was not erupted in a single phase because there are several distinct flows in a given section. For example, West, quoted by Mahapatra (1987), recorded 48 flows in three borings in the Deccan plateau of Eastern Saurashtra and Ahmedabad districts. The different flows are separated by ash beds/scoriae and lacustrine sediments which are called inter trappean beds. The maximum thickness of about 2000 m is attained around Bombay where the strata also show a gentle dip towards the Arabian Sea. The flows are practically horizontal otherwise and the thickness decreases towards the east.

The eruption of these lava flows marked an important event in the geological history of India. It is believed that the volcanism took place during the breakup of the ancient Southern continent of Gondwanaland about 60-100 Ma ago. Recent geological and tectonic investigations lead to the conclusion that the

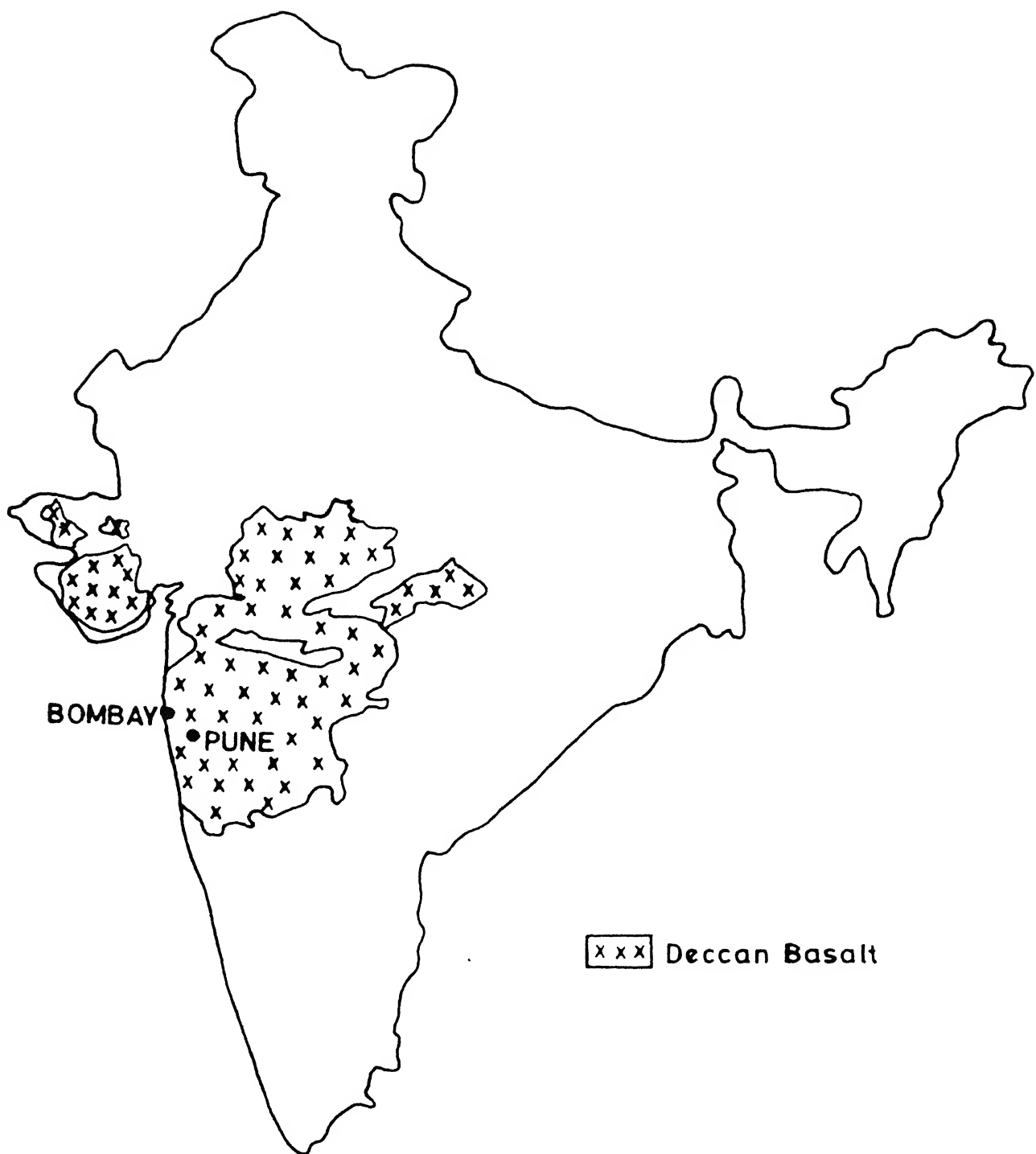


Fig. 2.1 Location map of Deccan Basalt

volcanism was mainly of the fissure type resulting in plateau basalt rather than eruption from isolated volcanic vents. Although local central type of flows have been advocated by some workers, the main volcanic activity is believed to have taken place along tectonic lineaments marked by i) the ENE-WSW trending Narmada-Son lineament-cum-graben belt, ii) the N-S trending Konkan and off-shore block faulted belt, and iii) the NNE-SSW trending Cambay graben belt (Krishnaswamy, 1981). The three major tectonic belts show positive gravity anomalies. It is well established that there are deep rooted faults and shear zones. From DSS study in Koyna, it was found that a fault is located near the dam site which extends upto 35 km which may have been the cause of seismicity in December 1967. Thermal springs are located parallel to these three belts. The thermal gradient is $43^{\circ} - 53^{\circ}\text{C/km}$ and the highest heat flow value of 2.25 HFU has been reported from the Cambay basin by NGRI. There also has been a recent hypothesis from NGRI that a meteorite impact caused Deccan volcanism.

Sukheshwala (1981) concluded that the first magma to erupt on a wide scale forming a major part of the Deccan Trap was of tholeiite type (silica rich basalt). This was followed by rhyolite in fairly large proportions and finally by minor quantities of alkali olivine basalt and Carbonatite magma. The range of chemical composition of 47 basalt flows in Mahad-Mahabaleshwar section given by Najafi et al. (1981) is summarized in Table 2.1.

Table 2.1

Range of Chemical Composition of Deccan Basalt in
Mahad-Mahabaleshwar Section (After Najafi et al, 1981)

Constituents	Range (Wt.%)
SiO_2	45.84 - 50.64
TiO_2	1.04 - 3.32
Al_2O_3	12.09 - 15.63
Fe_2O_3	4.23 - 9.24
FeO	4.68 - 10.92
MnO	0.09 - 0.40
MgO	4.50 - 7.07
CaO	7.54 - 11.41
Na_2O	1.90 - 3.83
K_2O	0.14 - 0.81
P_2O_5	0.08 - 0.63
Loss on Ignition	1.46 - 4.76

Trace Elements (ppm)

Ba	49 - 213
Rb	3 - 37
Sr	158 - 299
Zr	87 - 240
Nb	4 - 32
Y	23 - 55
Zn	70 - 136
Cu	91 - 271
Ni	74 - 145

For any discussion of the weathering of Deccan Basalt, it is important to estimate the time which elapsed between eruptions. Although this is a controversial topic, West (1981) quotes the description of the Bor Ghat section of Central Railway by Karmarkar (1978) where the flow surfaces appear to be unmodified by weathering or erosion. Both these authors, therefore, came to the conclusion that the eruptions took place in relatively rapid succession. West (1981) further states that weathering, in general, was limited to formation of red boles and laterites in a zone a few feet thick at the top of the flows. There was no time to develop any new topography.

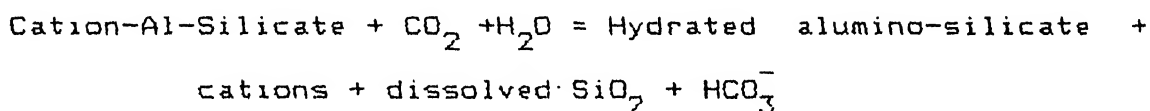
Subramanyan (1981) observed that spheroidal weathering, formation of blackish clay loam and fluvial erosion were the major geomorphic processes in the entire basalt country. He also noted sharp contacts between successive flows and ruled out the occurrence of any palaeosol in the weathering profile. Some more details on weathering are discussed in the next section.

2.2 Weathering Pattern of Deccan Basalt:

Weathering is the process of readjustment of rock forming minerals to present day environment at the surface of the earth. The minerals are usually in a state of disequilibrium due to the difference between the pressure and temperature of formation and earth surface conditions. In basalt, which is an igneous rock with a relatively high temperature of crystallization, the constituent minerals like olivine, pyroxene and Ca-rich

plagioclase are most unstable. They are, therefore, most weatherable as listed in the Goldich Weatherability Series discussed by Krauskopf (1979).

Among various natural agents of weathering, CO_2 -saturated water occurring as rain or ground water is most effective. The CO_2 is derived from the atmosphere as well as by the decay of organic matter in the soil zone. The weathering of a rock forming silicate mineral by natural water can be depicted as:



The net result of weathering of silicate rocks is thus an assemblage of clay minerals in soils and accumulation of dissolved ions in ground water. It has been observed that from a common parent rock like basalt, two types of residual soil profiles can be generated depending on the extent of removal of cations. When drainage is poor, the accumulated cations tend to form complicated structures of smectite group of clays. The soil is relatively dark in colour and has swelling properties (Black Cotton Soil). On the other hand, under extreme conditions of leaching, an assemblage of Al/Fe-oxides and kaolinitic clays gives rise to red coloured lateritic soils. The rate of weathering is relatively fast in humid tropical climate. This dual soil profile over basalt has been reported from various parts of the world. For example, Beckmann et al. (1974) during their study in Queensland, Australia reported red soils on top of the hills and black soil on

the pediment slope. Lunkad and Raymahashay (1978) also found black soil in the foot hills of Malwa plateau in the Deccan basalt province and lateritic soil at hill tops. They interpreted the ground water composition in terms of the thermodynamic stability of clay minerals which are products of weathering of plagioclase feldspar, pyroxene and volcanic glass. It was concluded that ground water in black soil zone has approached equilibrium with kaolinite and Ca-rich smectite. Pawar (1993) has discussed the mechanism of carbonate precipitation in basaltic aquifer due to weathering of plagioclase, augite and zeolite.

The occurrence of smectite in black soils contributes to some other properties like high plasticity and cation exchange capacity. It has been suggested that during dispersion of pollutants in ground water, black soils can provide effective barriers by cation absorption (Raymahashay, 1987)

2.3 Red Bole in Deccan Basalt:

In addition to red and black residual soils developing at the surface over Deccan basalt, a friable red horizon also commonly occurs in between two flows below the ground surface. This has been given the name Red Bole. Agashe et al. (1972) define this material (locally known as geru) as 'the peculiar, usually red, fine grained, clay like formation, occasionally seen amidst the Deccan traps'. These beds have been used as marker horizons in the field for differentiating one massive lava flow unit from another. For example, Najafi et al. (1981) found 35 red bole

layers among 47 flow units in the Mahad-Mahabaleshwar section. The composition of a typical red bole is given in Table 2.2.

Table 2.2

Composition of Red Bole at the Mula Dam site. From Agashe et al. (1972)

SiO ₂	54.8%
Al ₂ O ₃	18.8%
Fe ₂ O ₃	12.8%
CaO	3.7%
MgO	2.9%
Loss on Ignition	5.8%
Rest	1.2%

There is much controversy regarding the genesis of red boles. These are not typical 'inter trappean beds' of sedimentary origin. Earlier workers believed that these represent the soil derived by the weathering of the lower flow which was subsequently baked by the heat of the upper flow. For example, Pascoe (1964) has commented that the red colour is either due to heating of clays or represents relics of lateritic soil which develop over the lower basalt before they were covered by the upper basalt. He has also suggested that some red boles could have been formed by deposition of volcanic ash in water.

Agashe et al. (1972), on the other hand, are of the opinion that the red bole has been formed by the normal weathering of some variety of purple basalt and baking was not essential for their formation. The purple basalt, in turn, is believed to be the result

of hydrothermal alteration of an original dark basalt under the influence of magmatic gases. This idea has been further emphasized by Gupte (1992) in his text book where he traces the origin of red bole to hydrothermal alteration of a basalt glass (Tachylytic Basalt). He claims that the black tachylytic basalt changes to red tachylytic basalt under hydrothermal condition. Subsequently, on exposure to atmosphere, the red tachylytic basalt weathers to red bole. The friable red bole is believed to be restricted only to the surface and exposed faces.

Kshirsagar (1982) has tentatively suggested that the red boles are ash falls or ash flows (pyroclastic materials) which acquired their red colour due to oxidation of iron on exposure to atmosphere. This idea was proposed to explain their breccia like appearance particularly where they occur in association with highly zeolitized basalt lavas. Agashe et al. (1972) also noted that zeolitized basalt at the Mula dam site has fragments of purple rock separated from each other by zeolites giving the appearance of a volcanic breccia.

Because of their weathered nature and lack of strength, red bole layers cause problems in civil engineering construction. Very often excavation upto the underlying fresh basalt or removal by stripping has been recommended particularly at dam sites. Some representative engineering properties are listed in Table 2.3.

Table 2.3

Engineering properties of Red Bole. From Agashe et al. (1972) and Parthasarathy and Shah (1981)

Natural moisture content	15-18%
Natural dry density	1.44 - 1.69 gm/cc
Specific gravity	2.70 - 2.75
Apparent sp. gravity	2.20 - 2.30
Porosity	3.00
Water absorption	4.00
Liquid limit	55 - 60%
Plasticity Index	20%
Optimum dry density	1.40 - 1.52 gm/cc
Optimum moisture content	28 - 32%
Compressive strength	400 kg/cm ²
Modulus of Elasticity	1.00 x 10 ⁵ kg/cm ²
Ultrasonic pulse Velocity	2800 -3500 m/sec

Singhal (1973) observed that from a hydrogeological point of view, the red bole layers within the hard rock formations of the Deccan trap act as aquifers as well as confining layers depending on their texture and structure. When fractured and jointed, the red boles are good aquifers. On the other hand, a pink zeolitic basalt underlying a clayey red bole acts as a confined aquifer. Adyalkar and Suryanarayana (1976) concluded that red boles were relatively older weathering products and they also emphasized their importance in groundwater investigation.

As discussed below, the occurrence of zeolite within the red bole layer and as cavity filling in amygdaloidal basalt appears to be of great significance in terms of the origin of red boles as

products of hydrothermal alteration. Therefore, some details about the mineralogy of the zeolite group are reviewed in the next section.

2.4 Zeolites in Basaltic Rocks:

Zeolites are hydrated aluminosilicates of alkalies and alkaline earths. Their atomic structure is of the framework silicate type. Thus they are similar to the quartz-feldspar group. However, the structural framework of zeolites with large cavities is more open compared with feldspar. These cavities are responsible for some of the characteristic properties of zeolites like presence of water molecules, ion-exchange, and molecular absorption.

The structural formula of zeolites can be derived from a building block of $(\text{SiO}_2)_n$. Al^{3+} usually substitutes for Si^{4+} in the tetrahedral position and the net negative charge is balanced by cations like Na^+ , K^+ , Ca^{++} which are situated in the structural cavities (Deer et al., 1963). For example, the idealized formula of heulandite, $\text{Ca}_2(\text{Al}_4\text{Si}_{14})\text{O}_{36} \cdot 12\text{H}_2\text{O}$, a Ca-zeolite commonly found in Deccan basalt, is equivalent to $(\text{SiO}_2)_n \cdot x\text{H}_2\text{O}$ where $n = 18$ and $x = 12$. The charge deficiency due to substitution of four out of eighteen Si^{4+} by Al^{3+} is balanced by two Ca^{2+} ions.

The chemical composition of calcic zeolites differs mainly in the Al/Si ratio and H_2O content (Table 2.4). Coombs et al. (1959) classified the environment of formation of Ca-zeolites into three groups according to saturation with respect to silica. These are

1) supersaturated as in the case of heulandite, 2) saturated e.g. laumontite, and 3) under-saturated e.g. scolecite. The composition and occurrences of zeolites in the natural environment are, therefore, interrelated. Although authigenic zeolites have been reported from some sedimentary rocks, they mainly occur as 1) cavity filling in basalt, 2) products of hydrothermal alteration of primary silicate minerals in the lava flows and in country rocks of hot springs areas, and 3) products of extremely low grade metamorphism at temperature and pressure above diagenesis but below the green schist facies (Zeolite Facies of Coombs et al., 1959).

Table 2.4
Important Calcic Zeolites

Name	Composition	Al:Si
1. Heulandite	$\text{Ca}_2\text{Al}_4\text{Si}_{14}\text{O}_{36} \cdot 12\text{H}_2\text{O}$	1 : 3.5
2. Stilbite	$(\text{Na}, \text{Ca}) \text{Al}_2\text{Si}_6\text{O}_{16} \cdot 6\text{H}_2\text{O}$	1 : 3.0
3. Laumontite	$\text{Ca} \text{Al}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$	1 : 2.0
4. Chabazite	$(\text{Ca}, \text{Na}) \text{Al}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$	1 : 2.0
5. Scolecite	$\text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}$	1 : 1.5

Walker (1951) described the occurrence of zeolites in the plateau basalt of Ireland. He developed the concept of self generation of heat in the lava pile through exothermic reactions involving hydration of feldspar, olivine, and pyroxene. This led

to the formation of silica-poor zeolites like chabazite. The whole process took place much later than the eruption of the lava because considerable thickness of rock was required to accumulate sufficient heat. This idea was further extended by Walker (1960) in the basalt of Iceland where he concluded that the heat for zeolite formation was supplied by 1) later intrusion of dikes, 2) rise of heat from cooling of the lava, and 3) exothermic hydration reactions. He commented that below the water table, heated ground water reacts with basalt to produce zeolites. On the other hand, at the top blanket zone of basalt the temperature was too low to produce zeolitization.

Regarding the temperature of formation of zeolites, Walker (1951) suggested a value above 100°C . This can be considered in conjunction with the experimental data of Coombs et al. (1959) who concluded that in quartz bearing systems, Na and Ca-zeolites are not stable above 320°C .

A detailed work on zeolites in Deccan basalt exposed in the Bombay - Pune and Bombay - Nasik region was carried out by Sukeshwala et al., (1974). They mapped three principal depth zones namely, 1) laumontite at the lowest level starting from the coast, 2) scolecite at intermediate levels, and 3) stilbite-heulandite at the highlands near Pune. They concluded that the Ca-rich composition of zeolites reflected the composition of the host rock. As the zeolite zones were oblique to the lava stratigraphy, these authors advocated the later action of

circulating fluids in the basalt which gave rise to more hydrous and silicic variety at the top. On the other hand, laumontite at the base could be the result of burial metamorphism. Later work by Jeffery et al. (1988) has raised some doubt about the distribution of zeolite species according to elevation in the Bombay-Pune area.

Kostov (1981), after summarising various zeolite occurrences in Trap Volcanics, pointed out that the depth-wise sequence in Deccan basalt is different from that described by other workers. However, he emphasized that the zeolites are products of post volcanic hydrothermal solutions which may have been generated during the tensional deformation of the lava flows. The main factors controlling the composition of zeolites are Si/Al ratio, alkalinity of solution, temperature, and water pressure. He also recognized the possibility of descending water helping zeolite formation at depth.

CHAPTER 3

METHOD OF WORK

To achieve the objective of this thesis project the work was divided into two phases, namely, Field work and Laboratory work. These are discussed below:

3.1 Field Work:

The area of study falls in the hinterland of Pune City (Fig. 3.1). The field work was carried out in the last week of August, 1992, to study different rock and soil profiles and their natural relationship. Representative samples were collected from each for laboratory study. Two profiles were studied which are referred below as (A) the Shirwal Section and (B) the Saswad Section.

3.1A. Profile 'A'

It is located about 50 km from Pune towards Satara on N.H.4 near Shirwal town (Fig. 3.1). It is a road-cut near the proposed site of a new factory by the name of 'Lakim India Ltd.'. In this section only four horizons are exposed which can be described from bottom to top as lower basalt, red bole layer, upper basalt, and top soil.

3.1B. Profile 'B'

It is a ghat-section and occurs between Pune and Saswad on the Solapur road (Fig. 3.1). This section stretches for about 3 km. from Vadaki Nala (645 m above MSL), about 18 km from Pune and ends at Diva ghat temple (840 m above MSL). In this section, four red bole horizons were found interbedded with basalt flow units.

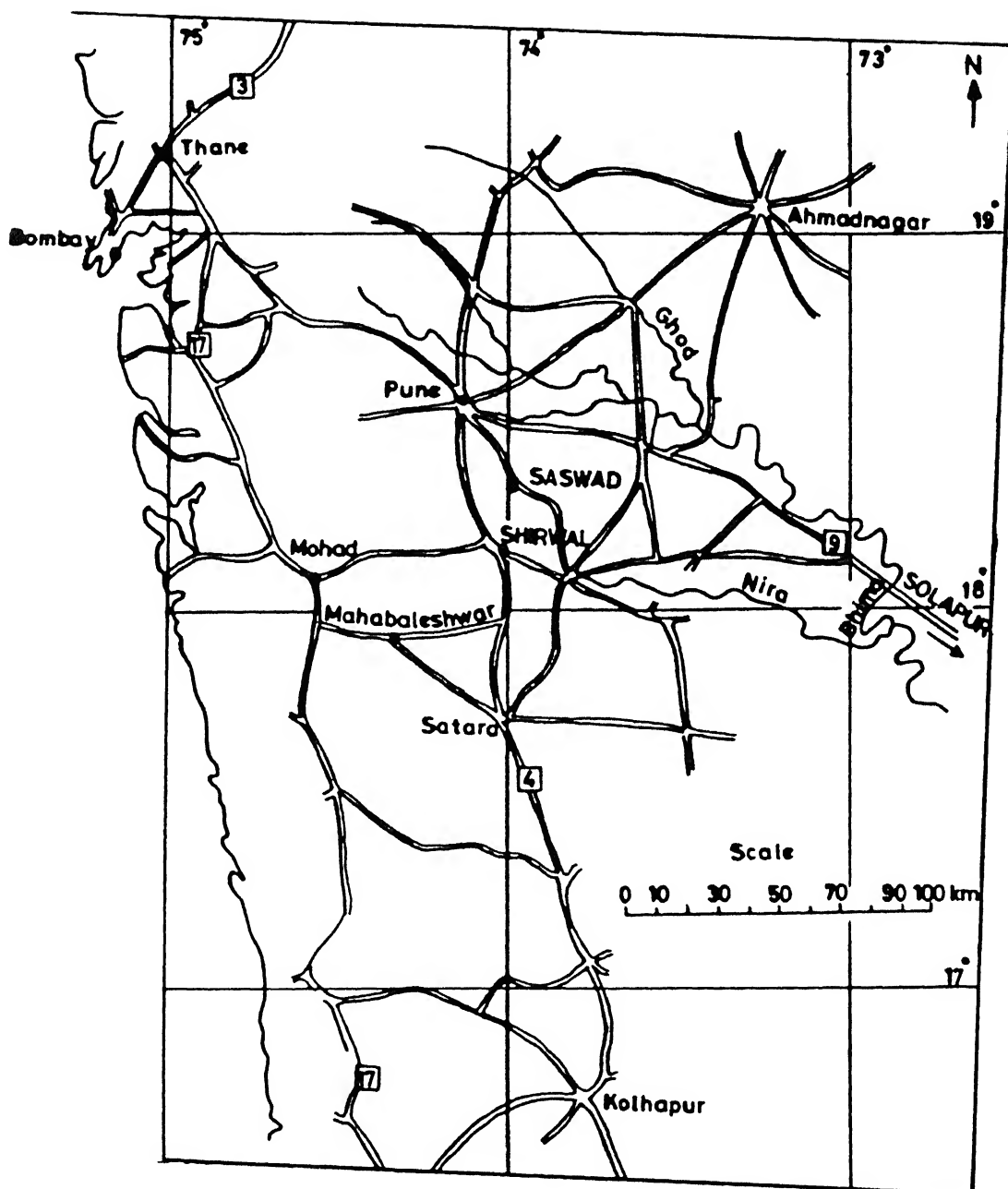


Fig. 3.1 Road Map of the study area

The results of field observations of these two sections are summarized in Chapter 4.

3.2 Laboratory Work

The samples collected in the field were of two types, namely, rock samples which are hard and tough, and soil samples in powder form. They were studied by the various methods described below.

3.2.1 Study of Rock Samples

1) In Hand-specimens

With the help of a binocular microscope (Bausch and Lomb) the rock samples were characterized according to grain size, colour, mineralogy, and texture etc.

11) In Thin Sections:

The thin section of rock samples were studied under petrographic microscope (Leitz) which helped in identification of the minerals which constitute the rocks. The properties like, colour, shape, cleavage patten, extinction angle, twinning and interference colour were used for differentiating individual minerals.

111) X-ray Diffraction:

The X-ray diffraction technique was used to establish the mineralogy of rocks. For X-ray diffraction rock powder was prepared from the rock sample with the help of mortar. All the powder and oriented slide sample were scanned on X-ray diffractometers Model ISO-DEBYFLEX-2002 (SEIFEORT) at 30 KV using Cr K_α radiation.

3.2.2 Study of Soil Samples:

i) Mineralogy:

The soil samples were first separated from roots, stems etc. After cleaning the soil samples, they were passed through different sieves to collect samples of controlled grain size for any analysis. It was done to maintain homogeneity. To establish the mineralogy of soil both bulk and oriented slides were run in X-ray diffractometer.

ii) Soil pH:

It was determined by using a SYSTRONICS DIGITAL pH METER. About 10 gm of sample was taken in a beaker and 1:4 suspension was made with distilled water. After stirring it was left for 1-2 minutes to settle and pH of the top layer of the solution was measured.

iii) Organic Matter Content:

About 2 gm of soil and 2-4 ml of distilled water were mixed to make 1:1 or 1:2 suspension in a 50 ml beaker. It was heated around 80°C and 30% hydrogen peroxide (H_2O_2) was added drop by drop while stirring. Its addition was continued until the sample ceased to froth. Then the sample was evaporated to dryness and weighed to constant weight after cooling.

iv) Cation Exchange Capacity (CEC):

In 50 ml of 4% HCl solution about 2 gm of sample was taken and left overnight. Next day it was filtered and washed chloride free using AgNO_3 . The washed sample was again put in 50 ml KCl

solution over night. Then next day it was filtered and the filtered solution was titrated with 0.01N NaOH solution using Phenolphthalein indicator. The exchangeable H^+ ion concentration was expressed in meq/100gm of sample.

3.2.3 Chemical Analysis:

It was carried out for only six radicals in the samples namely Na^+ , K^+ , Ca^{++} , Mg^{++} , total Fe and SiO_2 . Except for silica all other analyses were done by Atomic Absorption Spectrophotometer while for silica Cecil Spectrophotometer was used. Two types of solutions were prepared, namely, Solution 'A' for SiO_2 and solution 'B' for the other radicals.

Preparation of Sample Solutions:

Solution 'A'

About 0.025gm of the sample was taken in Ni-crucible with 3-4 NaOH pellets, and heated for 5 minutes until the NaOH melted. Again it was heated for 30 minutes at $55^\circ C$. After cooling, about 10 ml of distilled water was added and left overnight. Next day the solution were transferred to 250 ml. vol. flask and 5 ml 1:1 HCl with distilled water was added. After that the solution was heated so the solution became clear. Then the volume raised to 250 ml.

Analysis of SiO_2 :

About 8 ml of each sample solution, standard solution, and reagent blank solution were taken into 250 ml vol. flask. About 50 ml of distilled water and 2 ml of Amonium Molybdate (7.5 gm of

Amonium Molybdate in 75 ml of distilled water and 25 ml 1:4 H_2SO_4) were added in ech flask and left for 10 minutes. About 4 ml of Tartaric Acid was added by swirling the flasks (25 gm of the reagent in 250 ml of disttiled water) 1 ml of reducing agent was added and the volume of the solution kept upto 250 ml by adding distilled water. The sample solution were stirred properly and left for 30 minutes. (Reducing agent was prepared by dissolving 0.7 gm of Sodium sulfite in 10 ml water and then 0.15 gm of 1-amino-2-naphthol-4 sulfonic acid was added and stirred well until dissolved. 9 gm of Sodium bisulfite was dissolved in 90 ml of water and mixed with the first solution). The concentration was measured for standard as well as samples at 650 nm in Cecil Spectrophotometer.

Solution 'B'

It was used for the analysis of Na^+ , K^+ , Ca^{++} , Mg^{++} , and total Fe($Fe^{2+} + Fe^{3+}$). About 0.1 gm of sample in a Teflon bomb was taken and (0.5ml HNO_3 , 1.5ml HCl , 5ml HF) were added. The bomb was heated at $100^\circ C$ for $1\frac{1}{2}$ hrs or more until the solution was clear. Otherwise put it gain. About 1-15ml of distilled water was added and the solution kept in an oven for 1 hr. After that the solution was transferred to 100 ml volumetic flask and its volume raised to 100ml. This solution was run on Atomic Absorption Spectrophotometer.

CHAPTER 4

RESULTS AND DISCUSSION

To meet the objectives of this thesis, samples were collected from two profiles which are mentioned in the preceding chapter. The section at Shirwal was studied in greater detail. It is, therefore, described first. This is followed by comparative observations at the Saswad profile.

4.1 Description of Shirwal Profile:

This is a section exposed in a road cut near Shirwal town (see Fig. 3.1). There are four horizons on the vertical face of a hillock as seen in the photograph (Fig. 4.1). A rough sketch of the section along with sample locations has been provided in Fig. 4.2.

The lower most horizon is a highly weathered and zeolitized basalt which is called Lower Basalt in this report. The base is not seen and the exposed thickness is about 1.5m. It has a dominant purple colour speckled with white. The sample SHR(D) is soft and friable with coarse, granular texture due to crystals of zeolite and quartz which appear to fill tiny amygdales. The zeolite grains are tabular in shape and mainly transparent or white to light purple in colour. A black coating on the purple groundmass may be of organic origin.

The lower basalt is overlain by a brick red layer which is the true Red Bole. It is approximately 60 cm thick and is highly fractured and jointed. The contact with the lower basalt is



Fig. 4.1 Photograph of Shirwal Area

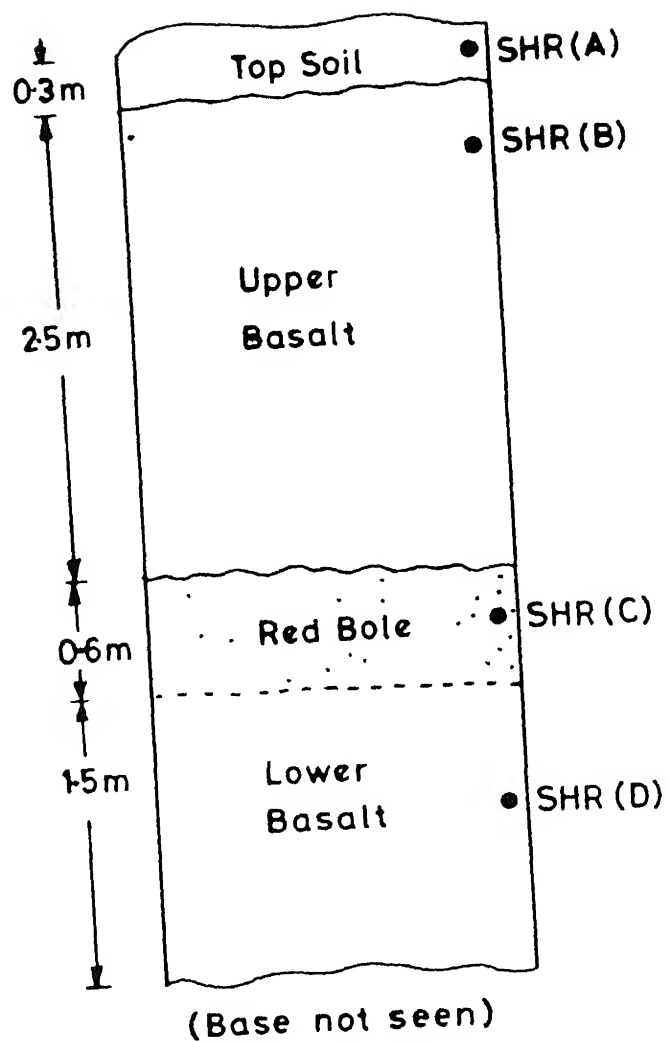


Fig. 4.2 Sample location of Shirwal section

gradational compared with a sharp upper contact with the basalt overlying the red layer. The sample SHR (C) collected during the monsoon period had a relatively high moisture content. It has a lumpy appearance due to fragments of a hard red material crisscrossed by white veins containing quartz and zeolite. The white minerals also seem to cement the red coloured rock fragments. Parts of the sample have a thin black coating possibly of organic matter.

The red bole layer is overlain by the Upper Basalt which is dark coloured and massive in nature. In the outcrop it shows columnar jointing and is highly fractured near its contact with the red bole below. The approximate thickness of this lava flow is 2.5m. In hand specimen, rounded dark grains occur within a fine grained grey matrix. These were later identified as altered olivine under the microscope.

A poorly developed Top Soil, about 30 cm thick, covers the upper Basalt. The soil is dark brown in colour and contains roots and organic debris along with fragments of basalt. These features indicate that soil development is at an immature stage.

4.2 Mineralogy of Shirwal Section:

The mineralogy of samples collected from the four horizons of the Shirwal section (see Fig. 4.2) was determined mostly from X-ray diffraction patterns. In addition, a thin section of sample SHR(B) from the upper Basalt was also studied under the petrological microscope.

It was observed that four minerals namely feldspar, quartz, pyroxene and iron oxide were common to all the four horizons although their proportions vary from one horizon to the other. Similarly, varying proportions of zeolite and smectite are present in the top soil, the red bole and the lower basalt. However, these two minerals were not detected in the X-ray pattern of the upper basalt.

The feldspar was identified to be a calcic plagioclase (bytownite) from its X-ray peaks at 6.51, 4.03, 3.79 and 3.19Å (strongest). From twinned feldspar laths in the thin section (Fig. 4.3), the extinction angle with respect to the (010) twin plane was measured to be around 25°. This corresponds to a plagioclase of An_{85} (bytownite) composition according to the determinative graph given by Wahlstrom (1955).

The X-ray peaks at 2.99, 2.56, 2.51, 2.94, 2.13 and 2.04Å matched with pyroxene of augite composition. Quartz showed characteristic X-ray peaks at 3.34 and 4.25Å. A peak around 2.69Å was attributed to hematite. Thin section and hand specimen of the upper basalt also showed an opaque mineral with cubic shape (Fig. 4.3) and magnetic property. From its association with hematite and X-ray peak at 2.94, 2.65 and 2.57Å, this mineral has been tentatively identified as maghemite.

Smectite showed a characteristic basal peak around 15Å in oriented slides which expanded to 17Å after glycolation. The sharpness of the peak varied in the different samples as discussed

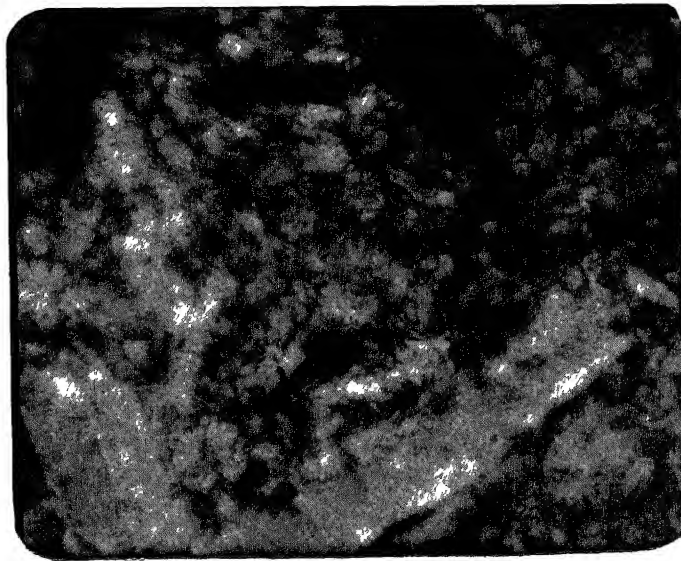


Fig. 4.3 Photomicrograph under X-nicols (400X)
of sample SHR(B)

later.

The zeolite has been identified as heulandite from its tabular crystal shape and transparent or white to light purple colour. Table 4.1 shows the identification on the basis of X-ray peaks. Absence of peaks at 4.08 and 4.68Å rules out stilbite which is a close associate of heulandite. Moreover, stilbite commonly occurs as twinned sheafs. This crystal habit was absent in the present samples.

Table 4.1

Comparison with standard X-ray peaks (Å) of zeolite minerals (Breck, 1974; Deer et al., 1963)

Stilbite	Heulandite	Observed in Red Bole
9.1,	8.90	8.95, 9.01
9.04	8.845	9.02
4.68,	-	-
4.07	-	-
-	3.917	3.90
	3.67	
3.41,	-	-
3.40		
3.20,		
3.19	-	-
3.03,		
3.04	-	-
-	2.97,	2.97,
	2.959	2.95

Table 4.2 summarizes the main features of the four samples and Fig. 4.4 is a comparative diagram of the major X-ray peaks. It is apparent that the lower most horizon and the red bole layer are similar in the sharpness of smectite, zeolite and hematite peaks. On the other hand, these peaks are diffuse or absent in the upper basalt and in the top soil. The poor development of smectite in the top soil and its absence in the upper basalt support the idea that the development of top soil by residual weathering of the upper basalt is at the initial stages. It was also observed that the 3.34\AA peak of quartz was strong and sharp in red bole indicating a relatively high proportion of this mineral. This feature of the red bole horizon is relevant for its possible origin by a hydrothermal alteration process.

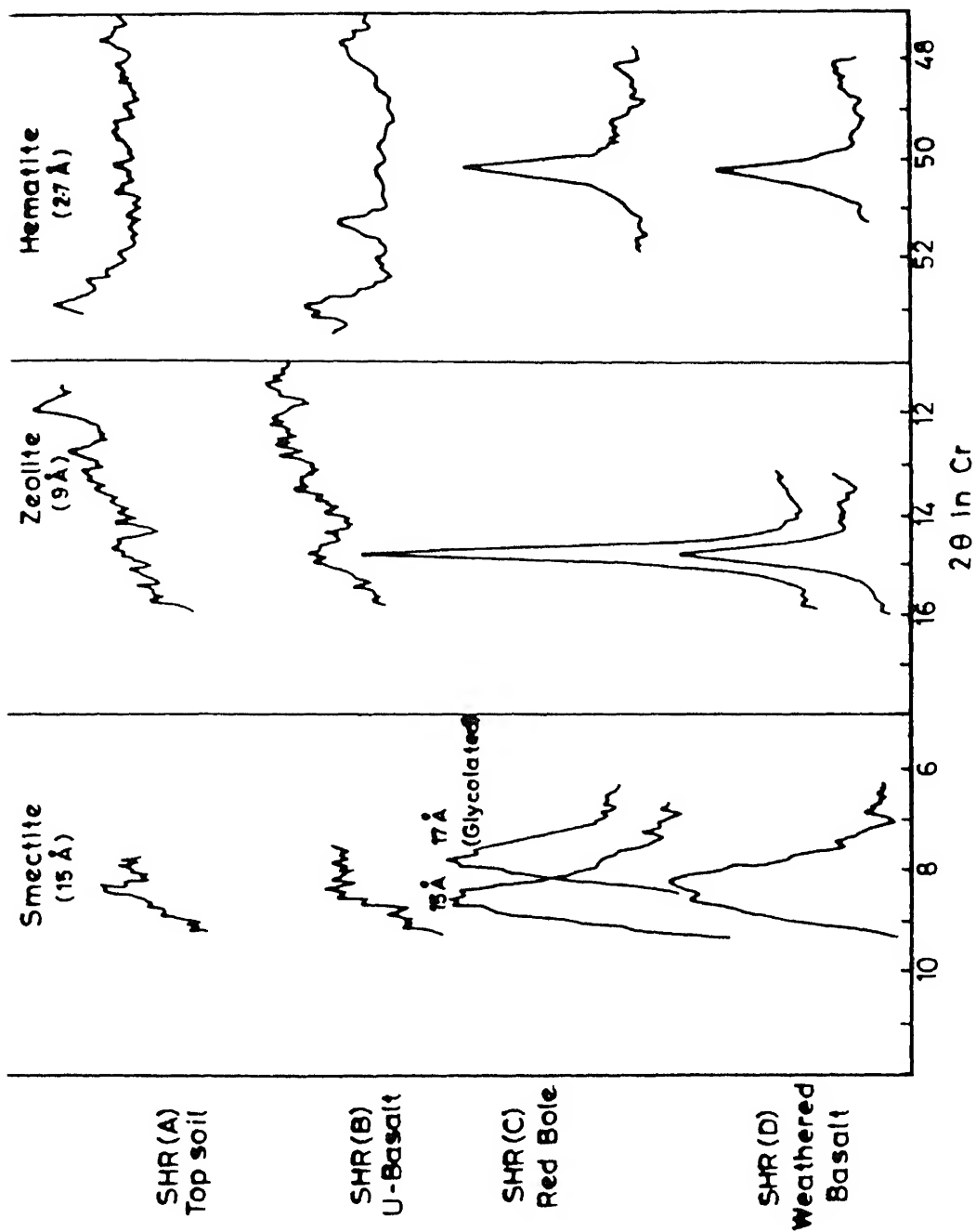


Fig. 4.4 Comparison of X-ray peaks at Shirwal

Table 4.2
Main Features of Shirwal Samples

Sample No.	Description	Relative height of x-ray peaks
SHR(A)	Top soil, Brown colour with organic debris and basalt fragments	Ca-plag \geq augite. Minor heulandite (8.89Å) smectite, hematite, quartz .
SHR(B)	Upper Basalt. Relatively fresh, massive, dark coloured	Ca-plag \geq augite. Minor hematite/maghemite, quartz
SHR(C)	Red Bole. Brick red colour. Hard and fractured. Fragments cemented by white minerals.	Quartz > heulandite (8.95Å) smectite > augite > hematite. Minor Ca-plag
SHR(D)	Lower Basalt. Highly weathered and zeolitized. Mostly zeolite and quartz crystals coating a friable, purple coloured ground mass.	Heulandite (8.97Å) > smectite > augite > Ca-plag > quartz

4.3 Selected Index Properties of Shirwal Profile

As described above, the Shirwal profile is relatively simple with four distinct mappable units in the vertical section. This allowed a detailed study to characterize the red bole horizon and to distinguish it from the top soils in terms of certain index properties like organic matter content, pH and Cation Exchange Capacity (CEC).

Table 4.3 summarises the results of analyses of the two samples SHR(A) and SHR(C). Although the top soil has developed over basalt, its CEC is much lower than the range of values

reported for Black Cotton Soil. It is possible that this reflects the lack of maturity of soil development as discussed in the previous section. For example, the relatively high CEC of Black Cotton Soil is usually attributed to the large amount of smectite present in this type of soil. However, the X-ray pattern of Shirwal top soil showed diffuse X-ray peaks of smectite indicating a low content of this mineral. The effect of organic matter on CEC also showed interesting result. As indicated in Table 4.3, the CEC decreased only marginally after removal of organic matter by H_2O_2 treatment. This shows that the organic matter content made up by roots and other organic debris does not contribute significantly to the bulk CEC of the soil. The measured CEC value is obviously due to the small amount of smectite and zeolite present in the soil.

Table 4.3

Index properties of Top Soil and Red Bole at Shirwal

	SHR(A) Top Soil	SHR(C) Red Bole
pH	7.5	7.95
Organic Matter	9.8%	-
CEC	16.2 me/100g (15 me/100g after removal of organic matter)	42.53 me/100g

Following the same line of argument, the relatively higher value of CEC in the red bole layer is consistent with sharp X-ray peaks of smectite and zeolite shown by sample SHR(C). The organic matter content is expected to be negligible at the depth of occurrence of this horizon. The relatively alkaline pH of the top soil and the red bole also matches with development of smectite by weathering of primary silicate minerals in the basalt.

Table 4.4 contains the analyses of major chemical constituents of the four horizons of Shirwal Section. No clear trend can be inferred from these data although certain broad generalizations are possible. For example, the SiO_2 and K content are of the same order of magnitude as reported by Najafi et al., (1981) for tholeiitic basalts of this area (see Table 2.1). The highest SiO_2 value of 59% in the red bole layer agrees with sharp X-ray peaks of quartz in sample SHR(C). It is possible that this quartz is a result of silica metasomatism during hydrothermal alteration. The high value of Fe (13.95%) in the layer also matches with the bright red colour and presence of sharp X-ray peaks of augite and hematite in this sample. On the other hand, the enrichment of Mg and Na between weathered lower basalt and red bole and also between upper basalt and top soil may reflect formations of smectite and presence of unaltered augite.

Table 4.4

Major Chemical Constituents of Shirwal Profile (wt %)

	Na	K	Ca	Mg	Fe	SiO ₂
SHR (A) Top Soil	1.57	0.31	1.20	1.02	13.2	51
SHR (B) Upper Basalt	1.12	0.31	1.68	0.48	16.4	54
SHR (C) Red Bole	1.07	0.13	1.41	1.31	13.95	59
SHR (D) Lower Basalt	0.57	0.17	1.38	1.10	14.7	52

4.4 Comparison with Saswad Profile:

As mentioned earlier, several outcrops of red layer interbedded with basalt were observed in the Divaghat - Vadki Nala section near Saswad. However, unlike the Shirwal section, there were no complete profiles containing all the four horizons of lower basalt, red bole, upper basalt and top soil. On the other hand, different combinations of these horizons were exposed at various elevations along the Ghat section stretching over a distance of 3 km. The samples collected from these outcrops were studied for their physical features and mineralogy without any chemical test. The main objective was to compare the occurrence of red boles with that observed at Shirwal.

The nature of exposures have been summarized in Figure 4.5. Table 4.5 contains a gist of the mineralogy as determined by X-ray diffraction. Fig. 4.6 compares the major X-ray peaks in various samples. These data indicate that although red coloured clayey horizons occupy interflow positions in the Saswad sections, there

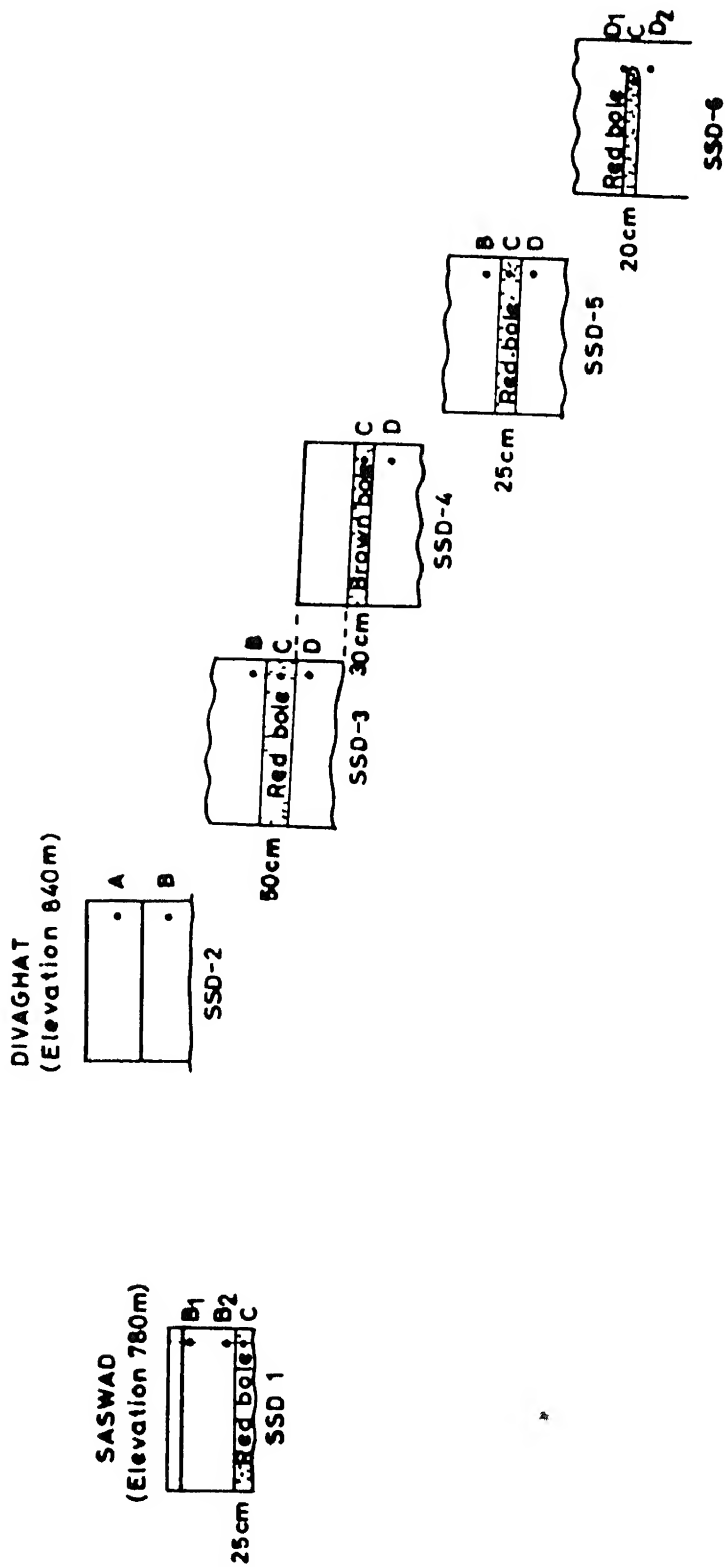


Fig. 4.5 Sample location of Saswad Section

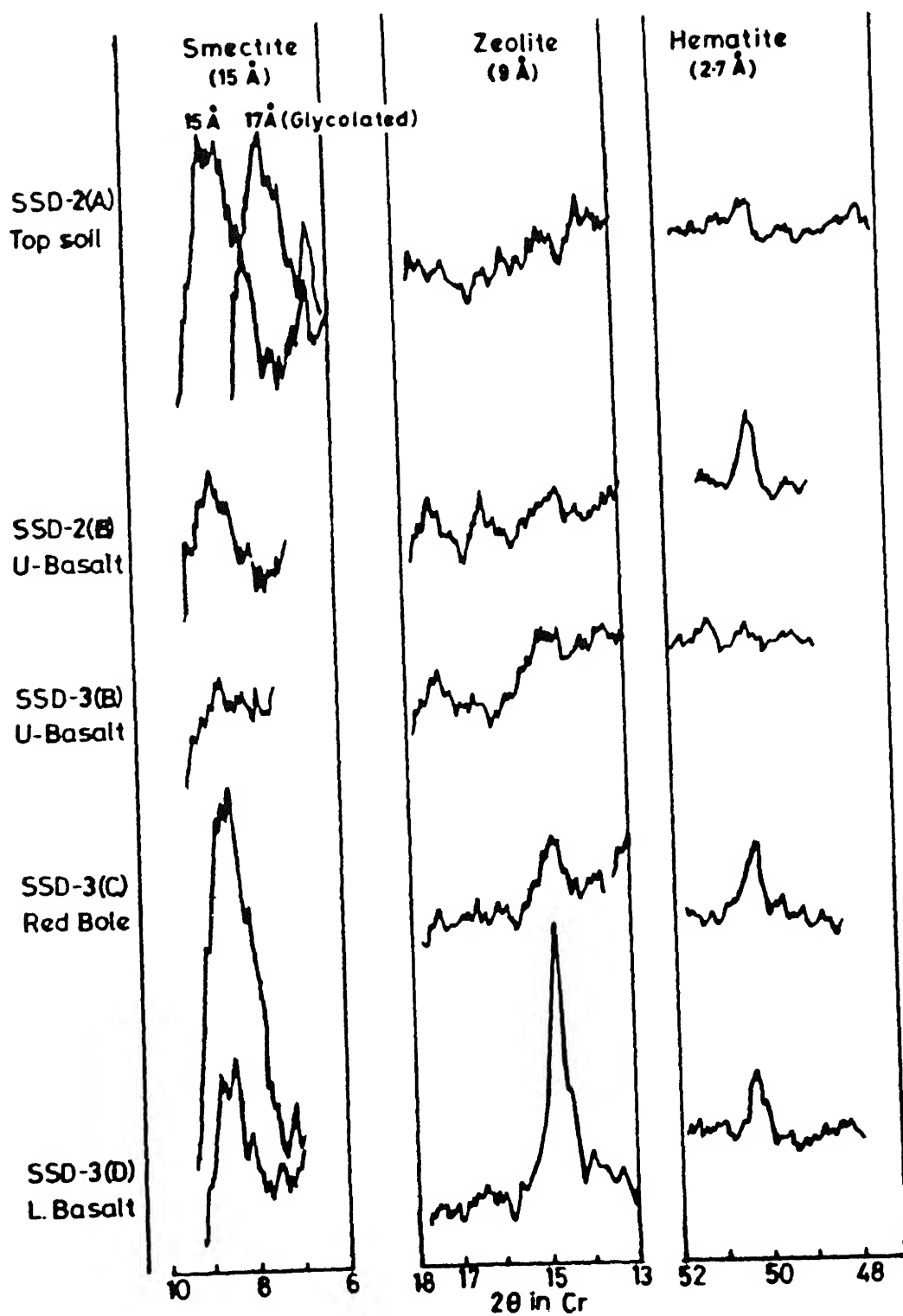


Fig. 4.6 X-ray peaks at Saswad

are basic differences with the red bole layer (sample SHR-C), occurring at Shirwal. (1) The red layer found above lower basalt or below upper basalt at Saswad contains unconsolidated granular material more like a soil rather than the hard, compact horizon at Shirwal. (2) While the Shirwal red bole is extensively cemented by quartz and zeolite veins, both minerals are rare or absent in all samples except SSD - 6(C). In fact, quartz does not show any major X-ray peaks in samples SSD-3 (C), 4(C) and 5(C). (3) On the other hand, like the Shirwal material, a frequent mineral in Saswad samples is smectite with a basal X-ray peak around 15\AA which expands to 17\AA on glycolation. (4) At least one sample i.e. 4(c) taken from the horizon between two basalt flows has a brown rather than red colour and is similar to the top soil, SSD 2(A), in its granular nature and high smectite content. (5) The smectite peak in the Saswad soil sample is sharper than that observed in the top soil at Shirwal. This suggests that the Saswad soil is comparatively more mature. In general, smectite is present in all horizons at Saswad including the weathered basalt flows. (6) On the other hand, zeolite of heulandite composition (8.7 to 9.0\AA X-ray peaks) is dominant only in the lower basalt e.g. SSD 3(D), 4(D) and 6(D). This is in contrast with the Shirwal section where heulandite was most dominant in the red bole horizon. (7) However, the contact between the red bole horizon and the overlying basalt is sharp (Fig. 4.7) at the Saswad section similar to the Shirwal occurrence. (8) Another general



Fig. 4.7 Photograph of Saswad area

observation is that some of the lower and upper basalt samples from Saswad e.g. SSD 6(D), SSD 5(D), and SSD 2(B) have a distinct chocolate brown colour compared with the grey colour of upper basalt at Shirwal. It is not confirmed whether this indicates a local compositional difference.

In summary, the red bole horizon at Shirwal can be distinguished from the local top soil by its physical properties and mineralogy. For example, the red bole horizon is different in colour and is a hard layer cemented by zeolite and quartz. However, the dark brown coloured top soil is loose, unconsolidated and has negligible content of zeolite and quartz. Although smectite is present in both horizons, the X-ray peak is sharper in the red bole.

The situation at Saswad is entirely different. The red layer in between the basalt flows is more like red soil rather than a compact rock. Moreover, there is no clear distinction between soil and red layer in mineralogy particularly with respect to quartz and zeolite content. Therefore, these red layers may not qualify as red bole in the true sense. Sample SSD 6(C) is the only exception. The red layer at this location is also relatively compact.

Table 4.5
Gist of Mineralogy of Sawad Section

	Description sample	Relative height of x-ray peaks
SSD-1 (B ₁) Upper Basalt away from the contact with red bole	Relatively fresh, Grey colour	Ca-plag >> augite Minor hematite, quartz, smectite and heulandite (8.98Å)
SSD-1 (B ₂) Upper Basalt near contact with red bole	Weathered, grey colour spotted white and iron stained	Ca-plag > augite > smectite minor hematite, quartz
SSD-1 (C) Red bole	Red Colour, granular Soft and friable	Smectite strongest. Minor hematite
SSD - 2 (A) Top Soil	Light brown, medium to fine grained, free of organic debris	Ca-plag ≥ smectite > augit > hematite = quartz
SSD - 2 (B) Upper Basalt	Chocolate brown colour, Amygdales filled with zeolite and quartz	Ca-plag > augite > hematit = smectite minor quartz an heulandite (9.07Å)
SSD - 3 (B) Upper Basalt	Dark Colour. Relatively fresh and massive, marginally amygdaloidal glassy in thin section	Ca-plag > augite minor hematite, quartz and smectite.
SSD - 3 (C) Red Bole	Red Colour. Soft and friable.	Smectite >> Ca-plag. = augite = smectite > hematite. Minor heulandite (8.92Å)
SSD - 3 (D) Lower Basalt	Purple colour. Amygdaloidal. Vesicles filled by transparent or white zeolite and light yellow clay mineral	Ca-plag > heulandite (8.95Å) > augite = smectite > hematite. Minor quartz

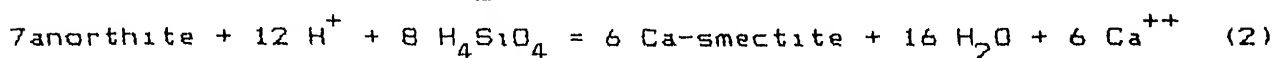
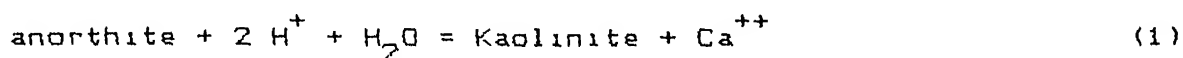
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Table 4.5 : Continued.

	Description sample	Relative height of x-ray peaks
SSD - 4(C) Brown Bole	Light brown, granular	Smectite strongest. Minor Ca-plag, augite quartz.
SSD-4(D) Lower Basalt	Grey, amygdaloidal, zeolite filling, dark grains of glass?	Ca-plag > heulandite (8.83Å) > augite. Minor smectite and quartz.
SSD-5(B) Upper Basalt	Relatively fresh, grey rock with dark spots (glass?)	Ca-plag >> augite Minor smectite and quartz.
SSD - 5 (C) Red Bole	Red, granular, soft and friable	Smectite >> Ca-plag = augite > hematite. Minor heulandite (8.77Å)
SSD - 5(D) Lower Basalt	Chocolate brown, amygdaloidal, zeolitic	Ca-plag >> augite > hematite. Broad smectite and trace of heulandite (8.72Å)
SSD - 6(C) Red Bole	Brick red colour. Weathered, friable with zeolite in pore spaces.	Heulandite (8.83Å) > smectite ≥ hematite > quartz > augite. Minor Ca - plag.
SSD-6(D ₁) Basalt above red bole lens	White shining crystals of zeolite on joint planes of chocolate brown basalt	Heulandite (8.8Å) > Ca-plag > augite > hematite, with trace of quartz and smectite
SSD - 6 (D ₂) Basalt below Red bole Lens	Weathered, reddish brown rock with dark particles (glass?) dispersed in ground mass. White or transparent zeolite filling a few vesicles	Ca-plag > heulandite (8.89Å) > augite > hematite. Minor quartz, smectite.

4.5 Weathering Reactions and Stability Diagrams:

It is well known that Deccan basalt contains highly weatherable components like volcanic glass, pyroxene and Ca-rich plagioclase. The formation of secondary clay minerals like kaolinite and smectite can be depicted by weathering reactions of the type listed below:



In these reactions, anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) represents the primary Ca-rich plagioclase present in fresh basalt. The H^+ ion stands for the mild acid derived from the dissolution of CO_2 in natural water which is the principal weathering agent. The soil smectite is represented by an idealised Ca-beidellite, $\text{Ca}_{\frac{1}{6}}\text{Al}_{\frac{2}{3}}\text{Si}_{\frac{2}{3}}\text{O}_{10}(\text{OH})_2$. The stoichiometry of the weathering reactions depends on the Al:Si ratio in the primary and secondary minerals because Al is assumed to be immobile during weathering. Therefore, Si in the form of dissolved H_4SiO_4 is added when Al: Si ratio is more in the weathering product as in reaction (2).

We can express the equilibrium constants of such reactions in terms of the thermodynamic activities of Ca^{++} ion, H^+ ion and dissolved silica (H_4SiO_4). Available free energy data then enable us to construct a stability diagram (Fig. 4.8) as proposed by Drever (1988) and earlier workers. The details for construction of this diagram are supplied in Appendix - I. This diagram shows that formation of smectite from feldspar requires higher silica

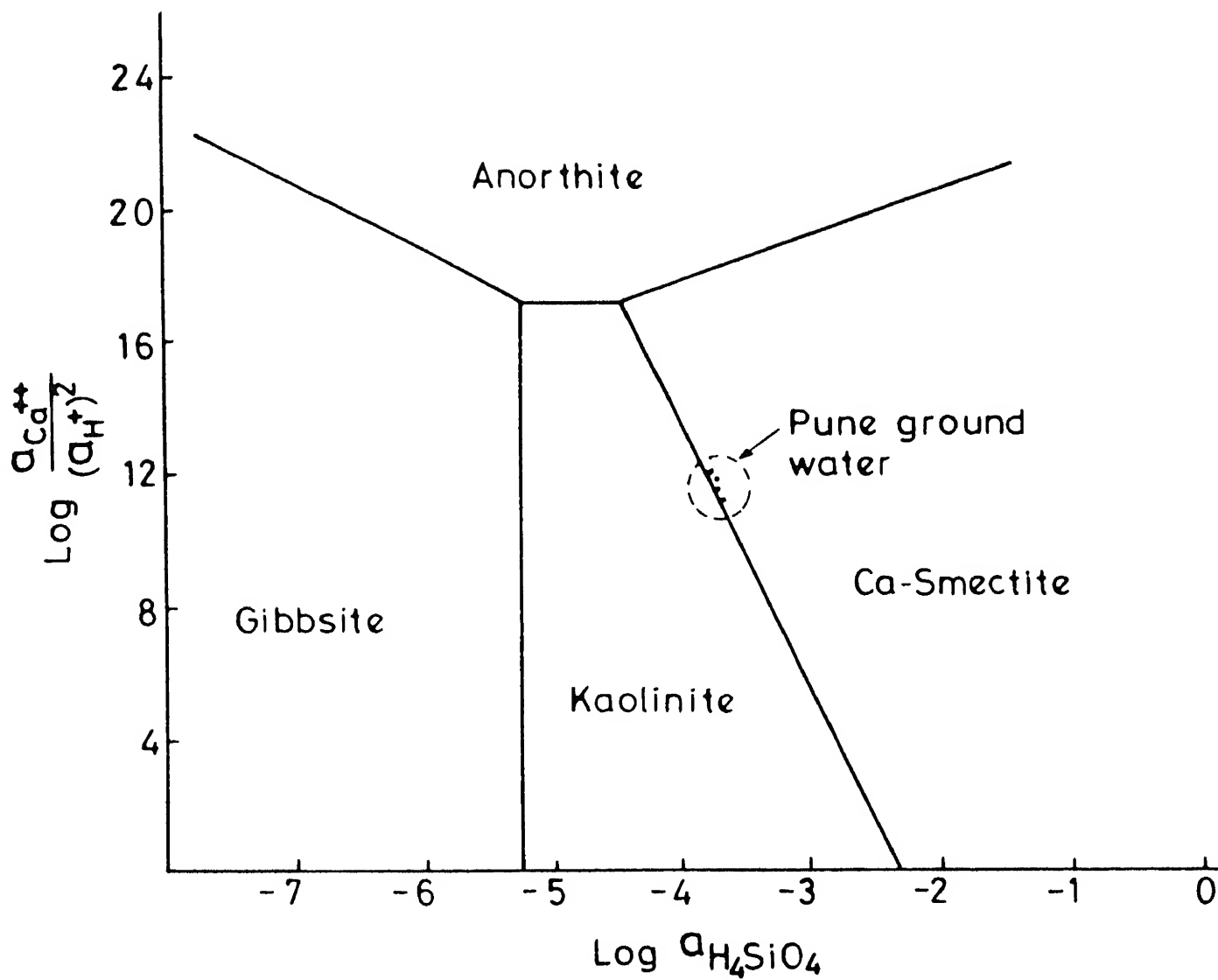


Fig. 4.8 Stability Diagram of Common Soil Minerals in the Ca-system

activity compared with kaolinisation of feldspar. This appears to be the controlling factor for the absence of kaolinite and presence of smectite in the profile under study. Although the exact composition of smectite has not been established, the Ca-rich nature of primary minerals makes it highly probable that Ca^{++} ion will be a prominent exchangeable ion.

Drever (1988) also included a field for zeolite represented by laumontite at high Ca^{++} activity and commented that other zeolites may be more stable than laumontite. This suggestion was followed up by utilising the free energy data for heulandite supplied by Woods and Garrels (1987) particularly because the zeolite in the present profiles has been identified as heulandite. The data in Appendix - II can be used to construct the stability diagram (Fig. 4.9) where the fields of gibbsite, smectite, kaolinite and heulandite are shown in the temperature range of 25°C to 100°C . A slightly different set of thermodynamic data (compared with Appendix - I) has been used to maintain internal consistency. The higher temperature range is relevant for the possible origin of heulandite by hydrothermal alteration of basalt.

Confirmation of the weathering reactions suggested above comes from analysis of ground water in the basaltic aquifers of Pune area recently reported by Pawar (1993). Table 4.6 summarises the analytical data of four samples where Si was determined. The ionic strength (I) calculated from the relation $I = \frac{1}{2} \sum m_i Z_i^2$ is

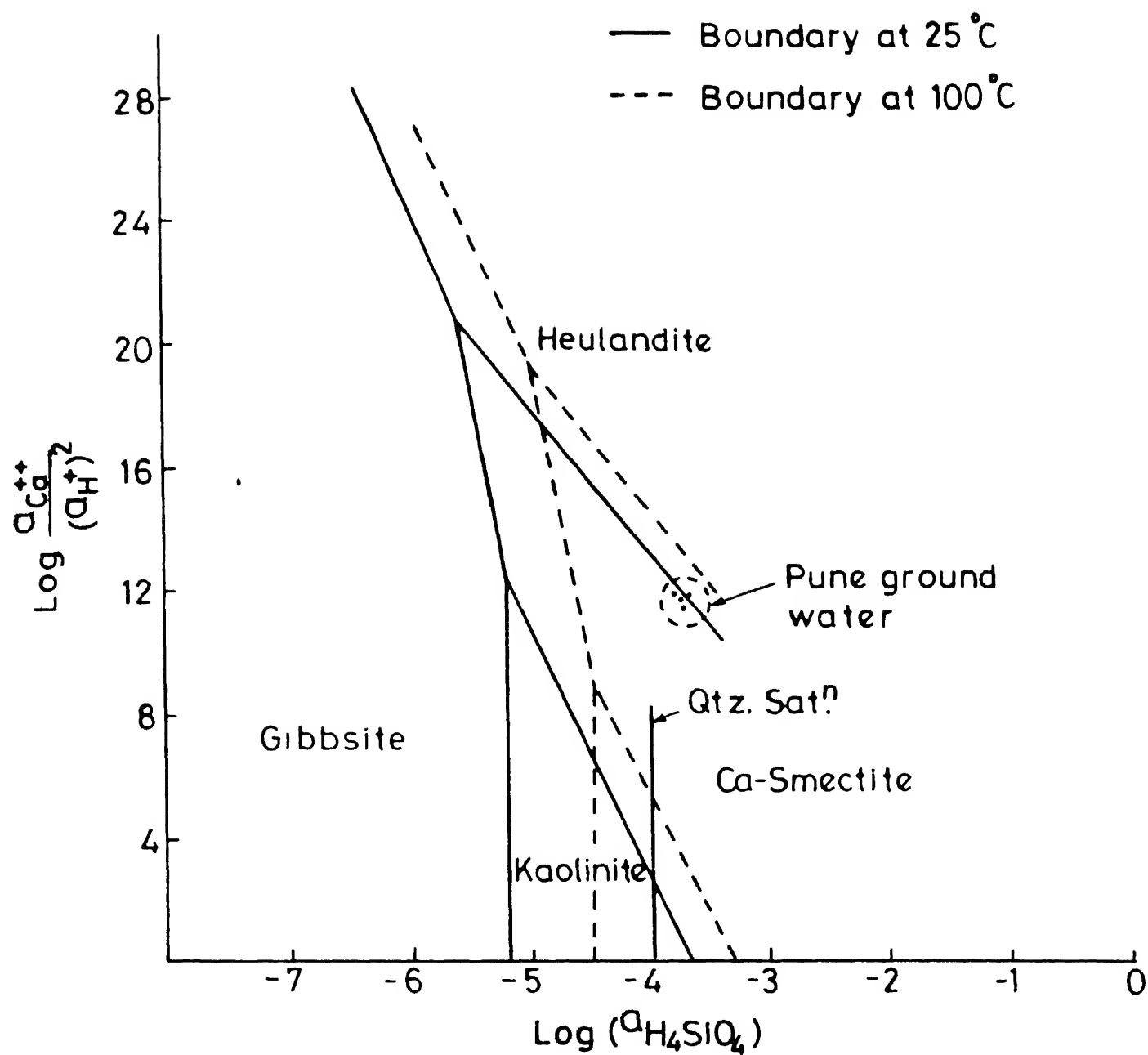


Fig. 4.9 Stability Diagram with Zeolite Field in the Ca-system

listed for each sample. The activity coefficient (γ) of Ca^{+2} ion was calculated at these ionic strength by interpolating the values listed by Krauskopf (1979) based on the Davies equation

$$-\text{Log } \gamma = AZ^2 \left[\frac{\gamma I}{1+\gamma I} - 0.2I \right]$$

where $A = 0.51$ in water at 25°C

Table 4.6

Chemical Analysis of Pune Ground water in millimole/L from Pawar (1993)

Sample No.	t ^o C	pH	Ca	Mg	Na	K	Cl	HCO ₃	SO ₄	Si
1	26	7.4	1.87	4.45	1.74	0.01	1.16	2.00	1.84	0.16
2	26	7.3	1.30	3.67	2.83	0.01	1.79	5.34	0.82	0.18
3	20	7.2	1.65	3.58	1.35	0.01	0.84	6.01	0.73	0.19
4	24	7.5	0.87	2.64	0.39	0.01	0.12	3.00	1.15	0.21

This gave the Ca^{++} ion activity $a_{\text{Ca}^{+2}} = \gamma_{\text{Ca}^{+2}} m_{\text{Ca}^{+2}}$ for each sample (Table 4.7). Similarly, a_{H^+} was calculated from the pH values ($\text{pH} = -\log a_{\text{H}^+}$). At the same time, the activity of the neutral dissolved silica species is given by $a_{\text{HSiO}_4} = m_{\text{H}_4\text{SiO}_4} = m_{\text{Si}}$. The values of $a_{\text{Ca}^{++}}/(a_{\text{H}^+})^2$ and $a_{\text{H}_4\text{SiO}_4}$ obtained by this procedure were then plotted on the two stability diagrams (Fig. 4.8 and Fig. 4.9). It is obvious that the ground water chemistry

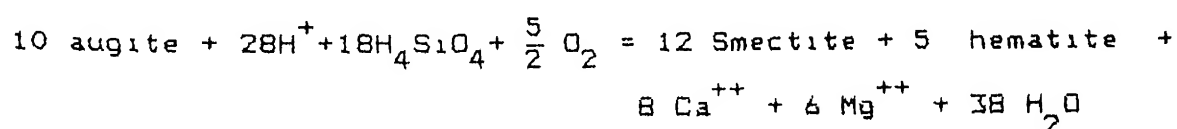
reflects equilibrium with an idealised Ca-smectite phase and water compositions plot very close to the Kaolinite - smectite and heulandite - smectite boundaries.

Table 4.7
Calculation of activities of Ca^{++} , H^+ and Silica

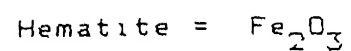
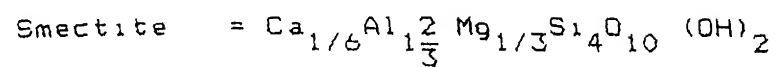
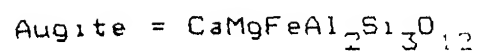
Sample No.	Ionic Strength	Ionic activity Coefficient $\gamma_{\text{Ca}^{++}}$	$a_{\text{Ca}^{++}} = \gamma_{\text{Ca}^{++}} \cdot m_{\text{Ca}^{++}}$	$a_{\text{H}^{++}}$	$\frac{a_{\text{Ca}^{++}}}{(a_{\text{H}^{++}})^2}$	$a_{\text{H}_4\text{SiO}_4}$
1.	0.018	0.61	$10^{-2.943}$	$10^{-7.4}$	$10^{11.86}$	$10^{-3.79}$
2.	0.0166	0.63	$10^{-3.087}$	$10^{-7.3}$	$10^{11.51}$	$10^{-3.74}$
3.	0.016	0.63	$10^{-2.983}$	$10^{-7.2}$	$10^{11.41}$	$10^{-3.72}$
4.	0.011	0.66	$10^{-3.241}$	$10^{-7.5}$	$10^{11.76}$	$10^{-3.68}$

These stability diagrams do not depict the weathering of pyroxene which is a common constituent of Deccan basalt. In fact, the weathering of pyroxene of augite composition is different from weathering of plagioclase in the sense that the former involves oxidation of Fe^{+2} to Fe^{+3} ion. In other words, this is an example of "Oxy-alteration" reaction resulting in typical red colour in altered basalt and residual soils.

A typical reaction for weathering of augite where Mg^{++} enters octahedral sites of a Ca-rich smectite and Fe^{++} is oxidized to hematite can be represented by



Where the idealised chemical compositions are:



It is obvious that this reaction will be controlled by silica activity as well as the partial pressure of O_2 gas.

CHAPTER 5

CONCLUSIONS

The Pune region can be considered as the type area for Deccan basalt outcrops. Field work was carried out at two locations, (1) Shirwal Satara road and (2) Saswad on Solapur road to collect samples of red layers occurring between basalt flows. The samples were studied in the laboratory to determine their mineralogy and other index properties. The main conclusions can be listed as follows:

- (1) The red layer at Shirwal occurs approximately 2.8 m below ground surface sandwiched between a dark coloured, massive upper basalt and a highly weathered and zeolitised lower basalt.
- (2) The thickness of the red layer is around 60 cm. Its upper contact is sharp whereas the lower contact is gradational.
- (3) The red layer, although weaker than the upper basalt in strength, is made of a hard and jointed material extensively veined and cemented by zeolite and quartz.
- (4) The properties of the zeolite match with heulandite. Sharp X-ray peaks of heulandite, quartz and a glycol expansive smectite distinguish the red layer from a thin dark soil cover on the upper basalt.
- (5) The abundance of heulandite and smectite possibly explains a high CEC value of the red layer compared with the top soil.

- (6) Recently available ground water analyses from this area indicate that heulandite and Ca-smectite are thermodynamically stable in the aquatic environment.
- (7) Some of the conclusions drawn at Shirwal do not hold true at the Saswad profiles. For example, the layer in between the basalt flow varies in colour from red to brown. The material is loose and unconsolidated and resembles a soil. There is no marked abundance of zeolite and quartz in the inter-flow layers. Therefore, a brown bole cannot be easily distinguished from the top soil.

The data from the limited number of samples described above do not resolve the controversy about the origin of red bole. The simplest definition of a red bole would be a red coloured clayey horizon occurring in between two basaltic lava flows at considerable depth below ground surface. On the other hand, the hypotheses regarding the origin of red boles vary from (1) formation of lateritic soil on an older lava flow, (2) baking of a palaeosol by the heat of the younger upper basalt eruption, (3) hydrothermal alteration of a black tachylitic (glassy) basalt to a red basalt which in turn weathers to red bole at the exposed surface (4) oxidation of pyroclastic material (ash bed) into iron oxide when exposed to the atmosphere.

The basalts of the study area do not contain a high proportion of glass and hence cannot be classified as 'tachylitic'. There is no clear evidence to conclude that the red coloured

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The basalts of the study area do not contain a high proportion of glass and hence cannot be classified as tachylitic. There is no clear evidence to conclude that the red coloured

material does not form a bed but has been derived from a red basalt by weathering on exposed surfaces only. Although the weathered lower basalt is commonly purple in colour, it is possible that the Ti content of augite and other constituent minerals is responsible for the colour. There are no high temperature mineral except zeolite which can also form under authigenic conditions in sedimentary rocks. If one accepts Walker's (1960) idea that zeolite forms at temperature above 100°C due to self generation of heat in a cooling lava pile, then the filling of amygdales by zeolite and quartz may be considered as a moderately high temperature (hydrothermal) process. The stability diagram (Fig. 4.9) shows that heulandite is stable at relatively higher silica activity. Quartz can precipitate under this condition. The relatively hard, quartz rich and zeolitized red layer at Shirwal in that case could be a true Red Bole.

The widespread occurrence of smectite in the samples studied, on the other hand, indicates low temperature weathering of primary silicates like Ca-plagioclase, augite and even secondary zeolite. The marked absence of kaolinite in the clay mineral assemblage may also reflect a relatively high dissolved silica activity (Figures 4.8 and 4.9). Development of recent top soil is at the initial stages, particularly at Shirwal.

Suggestions for Further Work:

Based on the knowledge gaps identified during the present study, further work along the following lines is suggested.

1. Determination of chemical composition and index properties of Saswad samples. The properties of the top soil and red bole horizons may be compared with the Shirwal samples.
2. Separation of zeolite crystals and further characterization by chemical analysis, XRD, and electron microscopy. This will help in identifying minor quantities, of other zeolite species, if any, in addition to the dominant heulandite.
3. Study of bore hole samples to prove the continuity or otherwise of the red coloured inter-flow layers.
4. Verification of the mechanism of alteration of zeolitic basalts through controlled laboratory experiments. The role of atmospheric O_2 may be studied in detail.
5. Investigation of the correlation, if any, between the variation in composition of primary basalts and properties of the inter-flow red bole horizons. Special attention should be paid to evidence of hydrothermal alteration.

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Appendix - I

Thermodynamic data used in the construction of the stability diagram (Fig. 4.8). ΔG_f° represents Gibbs energy of formation at Standard State i.e 298.15°K (25°C) and 100 K Pa (0.9869 atm).

Table A.I.1

Species	ΔG_f° (KJ/Mole)	Source
Gibbsite, $\text{Al}_2(\text{OH})_6$	-2309.78	Robie et al. (1978) ¹
Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	-3799.36	-do-
Anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$	-4017.266	-do-
Dissolved Silica, H_4SiO_4	-1307.74	Calculated from quartz Solubility = 6 ppm and ΔG_f° quartz = -856.29 (KJ/m)
Water, H_2O	-237.14	Robie et al. (1978) ¹
Ca^{++} ion	-553.54	-do-
Ca - Smectite, $\text{Ca}_{1/6}\text{Al}_{2/3}\text{Si}_{9/3}\text{O}_{10}(\text{OH})_2$	-5376.96	Calculated from log K = -18.4 for Kaolinite - Ca-Smectite equilibrium (Norton, 1974) ²

Ref.1: Robie, R.A., Hemingway, B.S. and Fisher, J.S. (1978) :
Thermodynamic properties of minerals and related substances
at 298.15K and 1 bar (10^5 pascals) pressure and at higher
temperatures. U.S. Geol. Survey Bull., 1452.

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Tanama system, West-Central Puerto Rico. Geochim. Cosmochim.
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Table A.I.2

Equilibrium reactions in the Ca-System at 25°C.

1. $\text{Kaol} + 5\text{H}_2\text{O} = \text{Gib} + 2\text{H}_4\text{SiO}_4$
 $\text{Log } K_1 = -10.478$
 $\text{Log } (a_{\text{H}_4\text{SiO}_4}) = -5.24$
2. $6 \text{Ca-smect} + 2\text{H}^+ + 23 \text{H}_2\text{O} = 7 \text{Kaol} + 8 \text{H}_4\text{SiO}_4 + \text{Ca}^{++}$
 $\text{Log } K_2 = -18.4$
 $\text{Log } \frac{a_{\text{Ca}^{++}}}{(a_{\text{H}^+})^2} = -18.4 - 8 \text{ log } a_{\text{H}_4\text{SiO}_4}$
3. $\text{Anor} + 2\text{H}^+ + \text{H}_2\text{O} = \text{Kaol} + \text{Ca}^{++}$
 $\text{Log } K_3 = 17.26$
 $\text{Log } \frac{a_{\text{Ca}^{++}}}{(a_{\text{H}^+})^2} = 17.26$
4. $\text{Anor} + 2\text{H}^+ + 6 \text{H}_2\text{O} = \text{Gib} + 2\text{H}_4\text{SiO}_4 + \text{Ca}^{++}$
 $\text{Log } K_4 = 6.78$
 $\text{Log } \frac{a_{\text{Ca}^{++}}}{(a_{\text{H}^+})^2} = 6.78 - 2 \text{ log } a_{\text{H}_4\text{SiO}_4}$
5. $7 \text{Anor} + 12 \text{H}^+ + 8 \text{H}_4\text{SiO}_4 = 6 \text{Ca-smect} + 16 \text{H}_2\text{O} + 6 \text{Ca}^{++}$
 $\text{Log } K_5 = 139.21$
 $\text{Log } \frac{a_{\text{Ca}^{++}}}{(a_{\text{H}^+})^2} = 23.20 + \frac{4}{3} \text{ Log } a_{\text{H}_4\text{SiO}_4}$

Appendix - II

Thermodynamic data used in the construction of the stability diagram (Fig. 4.9). ΔG_f° and S° represent standard state Gibbs energy of formation and entropy respectively.

Table A.II.1

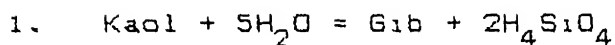
Species	ΔG_f° (KJ/Mole)	S° (J/Mole $^\circ$ K)	Source
Gibbsite, $\text{Al}(\text{OH})_3$	-1155	68.4	Helgeson et al 1978) ¹
Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	-3799.7	205.0	-do-
Ca - Smectite, ($\text{Ca}_{0.167}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$)	-5388.00	256.06	-do-
Dissolved Silica, H_4SiO_4	-1308.1	180.0	-do-
Water, H_2O	-237.13	69.91	-do-
Ca^{++} ion	-553.58	-53.6	-do-
Heulandite, $\text{CaAl}_2\text{Si}_7\text{O}_{18} \cdot 6\text{H}_2\text{O}$	-9754.7	-721.6	Woods & Garrels (1987) ²

Ref. 1: Helgeson, H.C., Delany, J.M., Nesbitt, H.W. and Bird, D.K. (1978): Summary and critique of the thermodynamic properties of rock-forming minerals. Am. J. Sci., vol. 278-A, pp. 1-229.

Ref. 2: Wood, T.L. and Garrels, R.M. (1987): Thermodynamic Values at Low Temperature for Natural Inorganic Materials - an uncritical summary. Oxford University Press, New York.

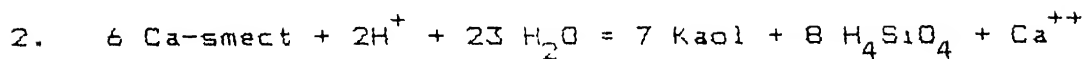
Table A.II.2

Equilibrium reactions in the Ca-System at 25°C and 100°C.



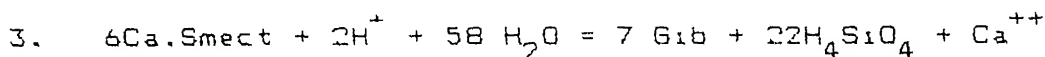
$$\text{At } 25^\circ\text{C} \quad \log a_{\text{H}_4\text{SiO}_4} = -5.18$$

$$\text{At } 100^\circ\text{C} \quad \log a_{\text{H}_4\text{SiO}_4} = -4.45$$



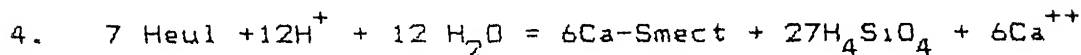
$$\text{At } 25^\circ\text{C} \quad \log \frac{a_{\text{Ca}^{++}}}{(a_{\text{H}^+})^2} = -29.04 - 8 \log a_{\text{H}_4\text{SiO}_4}$$

$$\text{At } 100^\circ\text{C} \quad \log \frac{a_{\text{Ca}^{++}}}{(a_{\text{H}^+})^2} = -26.63 - 8 \log a_{\text{H}_4\text{SiO}_4}$$



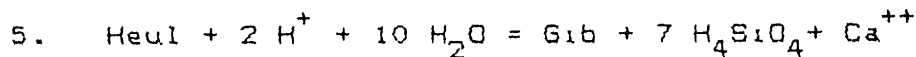
$$\text{At } 25^\circ\text{C} \quad \log \frac{a_{\text{Ca}^{++}}}{(a_{\text{H}^+})^2} = -101.59 - 22 \log a_{\text{H}_4\text{SiO}_4}$$

$$\text{At } 100^\circ\text{C} \quad \log \frac{a_{\text{Ca}^{++}}}{(a_{\text{H}^+})^2} = -88.96 - 22 \log a_{\text{H}_4\text{SiO}_4}$$



$$\text{At } 25^\circ\text{C} \quad \log \frac{a_{\text{Ca}^{++}}}{(a_{\text{H}^+})^2} = -4.68 - \frac{9}{2} \log a_{\text{H}_4\text{SiO}_4}$$

$$\text{At } 100^\circ\text{C} \quad \log \frac{a_{\text{Ca}^{++}}}{(a_{\text{H}^+})^2} = -3.42 - \frac{9}{2} \log a_{\text{H}_4\text{SiO}_4}$$



$$\text{At } 25^\circ\text{C} \quad \log \frac{a_{\text{Ca}^{++}}}{(a_{\text{H}^+})^2} = -18.52 - 7 \log a_{\text{H}_4\text{SiO}_4}$$

$$\text{At } 100^\circ\text{C} \quad \log \frac{a_{\text{Ca}^{++}}}{(a_{\text{H}^+})^2} = -15.64 - 7 \log a_{\text{H}_4\text{SiO}_4}$$

$$\text{Note:} \quad \log K \text{ at } 25^\circ\text{C} = \Delta G_r^\circ / -5.707$$

$$\Delta G_r^\circ \text{ at } 100^\circ\text{C} - \Delta G_r^\circ \text{ at } 25^\circ\text{C} = -\Delta S_r^\circ \cdot 75$$

$$\log K \text{ at } 100^\circ\text{C} = \Delta G_r^\circ / -7.13$$